# Interim Draft Guidance for Investigating Potential 1,2,3-Trichloropropane Sources in San Gabriel Valley Area 3

#### 1. Introduction

This document has been prepared to provide guidance to the United States Environmental Protection Agency (USEPA) Region 9 and the Los Angeles Regional Water Quality Control Board (LARWQCB) in locating potentially responsible parties (PRPs) who may have used the chlorinated volatile organic compound (VOC) 1,2,3-trichloropropane (1,2,3-TCP). An additional intended use of this document is to guide LARWQCB oversight of investigations at PRP facilities in San Gabriel Valley (SGV) Area 3 of the San Gabriel Basin Superfund Site in Los Angeles County, California, to assess potential releases of 1,2,3-TCP.

The body of this document provides a summary of background information on the identification of potential sources, investigation and sampling strategies, sampling methods, analytical methods, and remediation of 1,2,3-TCP contamination. Information on chemical properties, environmental fate and transport, uses and manufacturers, regulatory levels, documented occurrences of 1,2,3-TCP environmental contamination in the United States, and health risk information is provided in a series of appendices.

1,2,3-TCP is a synthetic (not naturally occurring) chemical that is a clear, colorless, dense, moderately volatile, moderately flammable liquid, described as having a sweet but strong acrid odor similar to chloroform. 1,2,3-TCP was previously used as a solvent, as a soil fumigant, and branching agent for polysulfide polymers. Alternate chemical names, chemical properties, and environmental fate and transport characteristics are provided in Appendix A. The California Department of Health Services (DHS) notification level (NL) for 1,2,3-TCP in drinking water is  $0.005 \,\mu\text{g}/\text{L}$ .

#### 2. Identification of Potential Sources

1,2,3-TCP occurs in groundwater in the central portion of SGV Area 3 at concentrations up to 413 ng/L (0.413  $\mu g/L$ ). The depth to groundwater in this portion of Area 3 ranges from approximately 275 to 300 feet below ground surface (bgs) as of January 2004. The subsurface alluvial sediments consist predominantly of sand and gravel, with minor amounts of silt and clay.

The source(s) of 1,2,3-TCP contamination in SGV Area 3 have not been determined to date. Because of the significant depth to water in the central portion of the OU, contaminant travel times between the ground surface and groundwater table, depending on the volume of a release (i.e., a large amount over a short duration or smaller quantities over a long duration), are expected to be on the order of tens of years. Therefore, sources (e.g., facilities) of potential concern include those that either have operated for many years (i.e. decades) or

have used large quantities of chemicals, or both. The previous existence of a "dry well" for disposal of relatively small quantities of liquid waste containing 1,2,3-TCP is another potential mechanism to explain the 1,2,3-TCP groundwater contamination in Area 3 (see Appendix D, MacKenzie Chemical Works site), although none have been identified.

Uses and manufacturers of 1,2,3-TCP are described in Appendix B. Based on this information, the types of businesses (e.g., facilities) that are considered to be potential release sources of 1,2,3-TCP are summarized in Table  $\underline{2}$ -1.

TABLE 2-1.
Uses of 1,2,3-TCP, Products, and Types of Businesses Using Products

Uses of 1,2,3-TCP	Products	Types of Businesses	Example Site or Source
Former (Historic) Uses			
Paint and varnish solvent	Paint and varnish	Paint manufacturer	
		Commercial painting facility	
Paint and varnish remover	Paint and varnish stripper	Solvent manufacturing or recycling facility	
	Furniture illistratiover	Paint stripping facility	
		Antique restoration facility	
Degreasing agent	Degreasing agent	Metals plating shop	Former MCAS Tustin, CAb
		Painting facility	
		Electronics manufacturer	
Soil fumigants of which	D-D	Agricultural applications	Central Valley, CA
1,2,3-TCP is a minor component	Telone II	Soil fumigants were used on citrus fruits, pineapple, soy beans, cotton, tomato, and potatoes.	
"Branching" agent for	Aircraft tank sealants	Aircraft manufacturers	San Fernando Valley
polysulfide polymers		Aircraft fuel tank manufacturers	Superfund Site (Area 1 - North Hollywood and Burbank-OU, CA)
		Aircraft maintenance facilities	
"Branching" agent for polysulfide polymers	Binder for rocket fuel	Rocket motor manufacturer	
		Rocket motor test facility	
Current Uses			
Chemical intermediate for synthesis of other	Polysulfone liquid polymers	Aerospace, automotive, consumer goods,	MacKenzie Chemical Works, NY
products	Polysulfides	electrical, electronic, health care and industrial equipment	YYOIRO, IVI
		Compressor and pump valve components	

TABLE 2-1.
Uses of 1,2,3-TCP, Products, and Types of Businesses Using Products

Uses of 1,2,3-TCP	Products	Types of Businesses	Example Site or Source <sup>a</sup>
Chemical intermediate for synthesis of other products	Hexafluoropropylene (key building block to produce Teflon fluoropolymers)	Agrochemical, electronics, dyes/pigments, pharmaceutical, and specialty polymer facilities	Ciba-Geigy, NJ
Chemical intermediate for synthesis of other products	Polysulfides (catalyst sulfidation agents, formulation of extreme pressure lubricant additives)	Lubrication product manufacturer	
Byproduct of the manufacture of epichlorohydrin	Over 80 percent of the 1,2,3-TCP manufactured in the U.S. is a byproduct of the manufacture of epichlorohydrin and is incinerated onsite	Petrochemical/industrial chemical complexes	
"Branching" agent for polysulfide polymers	Polysulfide polymer sealants	Window manufacturers	San Fernando Valley Superfund Site (Area 1 -
	Sealants for insulating	Boat manufacturers	North Hollywood and Burbank-OU, CA),
	glass windows	Adhesive manufacturer	<u>California</u>
	Construction adhesive		
	Boat hull sealants		
"Branching" agent for	Aircraft tank sealants	Aircraft manufacturers	San Fernando Valley
polysulfide polymers		Aircraft fuel tank manufacturers	Superfund Site (Area 1 - North Hollywood and Burbank OU, CA).
		Aircraft maintenance facilities	<u>California</u>

Notes:

Of the types of businesses that have historically used 1,2,3-TCP (Table 2-1), the most likely types of businesses to have operated in SGV Area 3 in the past are paint manufacturers, commercial painting facilities, paint stripping facilities, metal plating shops, electronics manufacturers, solvent manufacturer or recyclers, aircraft fuel tank manufacturers, rocket motor test facilities, and aerospace, automotive, compressor, and lubrication manufacturers.

# 3. Investigation and Sampling Strategies

A summary of site investigation tasks and descriptions is provided in Table <u>23-1</u>. Because of the chemical properties of 1,2,3-TCP (volatile, soluble, mobile), a combination of environmental media will need to be sampled to identify sources of 1,2,3-TCP groundwater contamination: soil, groundwater, and potentially soil gas (only if a true near-surface source

<sup>&</sup>lt;sup>a</sup>See Appendix D.

<sup>&</sup>lt;sup>b</sup>Associated with a former vehicle maintenance building.

area has been identified). Initiating site investigations through soil gas sampling may not produce data of sufficient quantity and quality to identify an area of a 1,2,3-TCP release, based on past experience in the <a href="San Fernando Valley Superfund Site">San Fernando Valley Superfund Site</a> (Area 1 - North Hollywood and Burbank-OU, also located in Los Angeles County), California (Tetra Tech, 2003).

**TABLE 23-1.**Summary of Investigation Tasks and Descriptions

#### Investigation Task

#### Description

Determine Study Area The investigation of 1,2,3-TCP sources <u>Study areas</u> should be focused on areas of <u>known 1,2,3-TCP release</u>, on <u>areas</u> that coincide with the location of regional 1,2,3-TCP groundwater contamination-or, <u>and on</u> areas that are <u>upup</u> gradient of existing regional contamination-based on current and historic groundwater flow directions.

The slope of interbedded subsurface sedimentary strata in the vadose zone may have also directed surface releases of 1,2,3-TCP to flow down slope, as it migrated through the vadose zone to the groundwater table; this migration direction may not eoincide with the regional groundwater flow direction.1,2,3-TCP migration may not immediately coincide with the regional groundwater flow direction but may first coincide with any preferential pathways of the subsurface strata in the vadose zone. In some cases, preferential flow of soil vapor in the vadose zone may be significantly different than preferential flow of groundwater in the saturated zone.

PRP SearchSearches and File Review (completed by the LARWQCB and EPA's PRP Search Contractor)Reviews

FocusPRP searches and file reviews should be focused on the types of operations/businesses listed in Table 2-1.

The business/operation may potentially be evaluated by looking for contaminants that occur with 1,2,3-TCP in soil and groundwater, as summarized in Table 3-2.

Review regulatory files at the Regional Water Quality Control Board (RWQCB), <a href="the-california">the-california</a> EPA\_- Department of Toxic Substances Control (DTSC), and <a href="the-city">the-city</a> Fire Department Hazardous Materials Management Unit for any evidence of 1,2,3-TCP use or release. Specific documents to be reviewed include <a href="the-material">the-material</a> safety data sheets (MSDS), hazardous materials business plans, and chemical inventory information.

Review site investigation reports (including Phase I environmental assessments, preliminary site investigations, subsurface investigations, hydrogeologic assessments, groundwater monitoring reports, soils investigations, underground storage tank (UST) and above-ground storage tank (AST) leak detection, investigation and closure reports, excavation reports, soil gas survey investigations, and soil and groundwater samples) that included 1,2,3-TCP as an analyte.

Review of Groundwater Monitoring Data In general, Groundwater in wells may need to be re-analyzed for 1,2,3-TCP (see Appendix C for additional detail on this topic) since 1,2,3-TCP was generally not included as an analyteanalyzed with low-level reporting limits until approximately 1999, when a DHS Action Level now referred to as the NLI was established. The detection limit for analysis of 1,2,3-TCP in groundwater prior to 1999 may be as high as 10  $\mu$ g/L, which is well above the current DHS NLI of 0.005  $\mu$ g/L. Therefore, retesting of wells may be required to assess the presence of 1,2,3-TCP in groundwater (see Appendix C for additional detail on this topic). 1,2,3-TCP may be detected as a tentatively identified compound (TIC) in historic monitoring data at concentrations exceeding approximately 90  $\mu$ g/L.

Soil Gas SurveySampling

Even though 200 µg/L of 1,2,3-TCP was detected in groundwater in a monitoring well near aircraft industry facilities in the Burbank OU, CA, 1,2,3-TCP was not detected in any of 54 soil gas samples collected at the facility (Tetra Tech, 2003) at a detection limit of 1 µg/L. Consequently, soil gas is currently anticipated to be of limited success as an approach to investigating potential 1,2,3-TCP releases based on prior experience in the Burbank OU. Evaluation of operations at a facility or

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# TABLE 23-1. Summary of Investigation Tasks and Descriptions

#### **Investigation Task**

#### Description

#### Determine Study Area

The investigation of 1,2,3-TCP sources Study areas should be focused on areas of known 1,2,3-TCP release, on areas that coincide with the location of regional 1,2,3-TCP groundwater contamination-or, and on areas that are upup gradient of existing regional contamination based on current and historic groundwater flow directions.

The slope of interbedded subsurface sedimentary strata in the vadose zone may have also directed surface releases of 1,2,3-TCP to flow down slope, as it migrated through the vadose zone to the groundwater table; this migration direction may not coincide with the regional groundwater flow direction.1,2,3-TCP migration may not immediately coincide with the regional groundwater flow direction but may first coincide with any preferential pathways of the subsurface strata in the vadose zone. In some cases, preferential flow of soil vapor in the vadose zone may be significantly different than preferential flow of groundwater in the saturated zone.

PRP SearchSearches and File Review (completed by the LARWQCB and EPA's PRP Search Contractor)Reviews FocusPRP searches and file reviews should be focused on the types of operations/businesses listed in Table 2-1.

The business/operation may potentially be evaluated by looking for contaminants that occur with 1,2,3-TCP in soil and groundwater, as summarized in Table 3-2.

Review regulatory files at the Regional Water Quality Control Board (RWQCB), <a href="the-california">the-california</a> EPA\_- Department of Toxic Substances Control (DTSC), and <a href="the-city">the-city</a> Fire Department Hazardous Materials Management Unit for any evidence of 1,2,3-TCP use or release. Specific documents to be reviewed include <a href="the-material">the-material</a> safety data sheets (MSDS), hazardous materials business plans, and chemical inventory information.

Review site investigation reports (including Phase I environmental assessments, preliminary site investigations, subsurface investigations, hydrogeologic assessments, groundwater monitoring reports, soils investigations, underground storage tank (UST) and above-ground storage tank (AST) leak detection, investigation and closure reports, excavation reports, soil gas survey investigations, and soil and groundwater samples) that included 1,2,3-TCP as an analyte.

business should be known, so that collection of soil gas samples can be focused on those areas where elevated subsurface concentrations associated with a release are likely to occur, thereby enhancing the success of an investigation. Soil gas surveys are currently anticipated to be of limited success as an approach for investigating potential 1.2.3-TCP releases. Therefore, soil gas surveys should be based on an evaluation of prior facility operations and should subsequently be focused in areas where 1.2.3-TCP releases are likely to have occurred. The need for focused soil gas surveys is based on prior experience at the San Fernando Valley Superfund Site (Area 1 - North Hollywood and Burbank), where 1,2,3-TCP was detected at a concentration of 200 µg/L in aircraft facility groundwater but was not detected in 54 soil gas samples collected at the facility (Tetra Tech, 2003).

# TABLE 23-1. Summary of Investigation Tasks and Description

Investigation Task	Description
Determine Study Area	The investigation of 1,2,3-TCP sources <u>Study areas</u> should be focused on areas of known 1,2,3-TCP release, on areas that coincide with the location of regional 1,2,3-TCP groundwater contamination or, and on areas that are upup gradient of existing regional contamination based on current and historic groundwater flow directions.
	The slope of interbedded subsurface sedimentary strata in the vadose zone may have also directed surface releases of 1,2,3-TCP to flow down slope, as it migrated through the vadose zone to the groundwater table; this migration direction may not coincide with the regional groundwater flow direction-1,2,3-TCP migration may not immediately coincide with the regional groundwater flow direction but may first coincide with any preferential pathways of the subsurface strata in the vadose zone. In some cases, preferential flow of soil vapor in the vadose zone may be significantly different than preferential flow of groundwater in the saturated zone.
PRP SearchSearches and File Review (completed by the	FocusPRP searches and file reviews should be focused on the types of operations/businesses listed in Table 2-1.
LARWQCB and EPA's PRP Search Contractor)Reviews	The business/operation may potentially be evaluated by looking for contaminants that occur with 1,2,3-TCP in soil and groundwater, as summarized in Table 3-2.
<del>Contractor <u>I</u>\teviews</del>	Review regulatory files at the Regional Water Quality Control Board (RWQCB), the California EPA - Department of Toxic Substances Control (DTSC), and the City Fire Department Hazardous Materials Management Unit for any evidence of 1,2,3-TCP use or release. Specific documents to be reviewed include the material safety data sheets (MSDS), hazardous materials business plans, and chemical inventory information.
	Review site investigation reports (including Phase I environmental assessments, preliminary site investigations, subsurface investigations, hydrogeologic assessments, groundwater monitoring reports, soils investigations, underground storage tank (UST) and above-ground storage tank (AST) leak detection, investigation and closure reports, excavation reports, soil gas survey investigations, and soil and groundwater samples) that included 1,2,3-TCP as an analyte.
Subsurface Soil Sampling	The traditional approach of collection and analysis of in situ subsurface soil samples by direct push, cone penetrometer test (CPT), hollow-stem auger drilling with a California modified soil sampler or equivalent, or collection of drive Because the detection of 1,2,3-TCP may be limited to small stratigraphic lenses over short intervals, as observed in San Fernando Valley Superfund Site (Area 1 - North Hollywood and Burbank) (Tetra Tech, 2003), soil samples should be collected and analyzed every 5 to 10 feet over the entire depth of a boring. Alternatively, select soil samples through drill casing using air rotary/casing drive is recommended.
	Because detections of 1,2,3-TCP may be limited analyzed according to thin (approximately 10-foot) depth intervals, as observed in the Burbank OU (Tetra Tech, 2003), samples should be collected and analyzed every 5 to 10 feet over the entire depth of the boring, or samples identified by detection of elevated head space readings (_as_measured with an organic vapor analyzer [(OVA]) should be analyzed for 1,2,3-TCP-) or flame ionization detector (FID).
	The traditional approach for collecting and analyzing <i>in situ</i> subsurface soil samples by direct push methods, a California modified soil sampler, or equivalent is recommended.
Groundwater Sampling	Collect groundwater Groundwater samples for 1,2,3-TCP analysis should be collected from existing monitoring and production wells.
	Install, and new monitoring wells in should be installed at key locations to help further refine the interpreted extent of 1,2,3-TCP in groundwater-contamination.

The occurrence of 1,2,3-TCP with other contaminants in soil or groundwater may in some cases assist in determining the source of 1,2,3-TCP in soil or groundwater, as summarized in Table  $3\underline{-2}$ .

TABLE 3-2.
Comparison of Contaminants to Potential Businesses/Operations

Contaminants Detected in Groundwater	Potential Business/Operation (see Appendix B)
1,2,3-TCP only	Painting or paint stripping, aviation/fuel tank sealing, boat construction facilities, compressor and pump maintenance/manufacturing
1,2,3-TCP with trichloroethene (TCE), tetrachloroethene (PCE)	Metal or plastics plating facility, paint stripping facility, painting facility, aviation/fuel tank sealing, automotive manufacturing, mechanical maintenance shop
1,2,3-TCP and perchlorate	Aerospace/rocket motor production, testing, and disposal
1,2,3-TCP with 1,2-dichloropropane or 1,2-dibromo-3-chloropropane	Agricultural application (especially citrus) of soil fumigant; storage or distribution center off agricultural chemicals

# 4. Sampling Methods

Recommendations for sampling methods for collection of soil, groundwater, and soil gas samples for 1,2,3-TCP analyses are provided in this section. All sampling methods are listed and briefly described in Table  $4\underline{-1}$ . Following this table, Sections 4.1, 4.2, and 4.3 provide additional details on specific issues pertaining to sampling of each media. Analytical methods are provided in Section 5.

TABLE 4-1 1,2,3-TCP Sampling Method

Media	Sampling Method	Sample Container
Groundwater		
Groundwater – in situ samples	HydroPunch™ sampler, (collect groundwater sample with small diameter bailer inside HydroPunch assembly, decant to VOA vial)	40-ml VOA vial, HCl to pH <2, no headspace, cooled to $4^{\circ}\text{C}$
	BAT™ system groundwater sampler (evacuated 120-ml glass vial) is filled when septa is punctured in the subsurface	Cool glass vial to 4°C immediately upon retrieval, submit to lab for analysis
	SimulProbe™ (able to collect simultaneous soil and groundwater samples)	Immediately transfer liquid sample to 40-ml VOA vial, HCl to pH <2, no headspace, cool
	<b>NOTE:</b> Use of in situ, depth-specific samples permits characterization of the vertical extent of 1,2,3-TCP contamination.	to 4°C  NOTE: Given the depth to groundwater in SGV Area 3 (275 to 300 feet bgs), the cost to collect in situ groundwater samples below the water table may be cost prohibitive.

**TABLE 4-1** 1,2,3-TCP Sampling Methods

Media	Sampling Method	Sample Container
		Depending on the depth of sample collection, these in situ methods may need to be used in combination with subsurface drilling methods.
Groundwater – production wells	Fill sample container directly from wellhead tap, taking care to minimize sample aeration.	40-ml VOA vial, HCl to pH <2, no headspace, cool to $4^{\circ}\text{C}.$
Groundwater - monitoring well	Dedicated pump (low-flow method preferred)	Directly fill 40-ml VOA vial, HCl to pH <2, no headspace, cool to 4°C
	Diffusion bag sampler(s) (allow to equilibrate per instructions)	Carefully decant sample(s) into 40-ml VOA vial(s), HCl to pH <2, no headspace, cool to
	NOTE: With the aide of multiple	4°C
	samplers, a vertical concentration profile may be obtained.	NOTE: Vroblesh and Campbell (2001) report that when using polyethylene based passive diffusion samplers for VOCs, the concentrations of 1,2,3-TCP measured with the diffusion bag sampler was within 10 percent of the concentration in ambient water.
Multiple-port groundwater monitoring well	Use Westbay sampling equipment to collect groundwater sample	Fill 40-ml VOA vial directly from Westbay sample container, HCl to pH <2, no headspace, cool to 4°C
Soil		
Soil - surface	Sample directly sample with Encore sampler	Encore sampler, cooled to 4°C
	Collect grab sample with stainless steel spade, pack soil tightly into jar.	4-ounce glass jar (no headspace), cooled to $4^{\circ}\text{C}$
Soil – subsurface	Direct push sampler	Brass or stainless steel (SS) sample sleeve;
	Piston sampler	seal end with Teflon tape, foil, and plastic end caps; cooled to 4°C
	California modified soil sampler	
	SimulProbe™ (able to collect simultaneous soil and groundwater or soil and soil gas samples)	
Soil Gas		
Soil Gas	Install temporary or permanent soil gas sampling probe, purge, and sample per LARWQCB/DTSC guidance (2003)	Syringes, glass bulbs wrapped in Aluminum foil, SUMMA™ canisters

#### 4.1 Groundwater

Groundwater samples may be collected from production wells, conventional groundwater monitoring wells, multiple port monitoring wells, and with diffusion bag samplers. In-situ (depth-specific) groundwater samples may be collected to characterize the vertical extent of 1,2,3-TCP groundwater contamination.

#### **Monitoring Wells**

Sample collection from conventional and multiple port monitoring wells is the most common and direct method for detecting and monitoring 1,2,3-TCP in groundwater. A low-flow method sampling method is recommended to minimize 1,2,3-TCP losses due to volatilization from turbulence within the well and during filling of sample containers. Samples collected in this manner are will yield laboratory analytical results that are considered to be more representative of actual in situ groundwater concentrations.

#### **Diffusion Bag Samplers**

Vroblesh and Campbell (2001) reported that when using polyethylene based passive diffusion samplers for VOCs, concentrations of 1,2,3-TCP measured in samples collected with the diffusion bag sampler were within 10 percent of the concentrations in ambient water. This close agreement indicates that diffusion bag samplers are a viable alternative for collection of groundwater samples for analysis of 1,2,3-TCP. If a series are bags are suspended at different depths in a well, a vertical profile of 1,2,3-TCP concentrations may be obtained, assuming that the well is not acting as a conduit for vertical groundwater flow (which would result in non-representative samples). This method is best suited for detailed profiling in wells with relatively short (i.e., 50 feet or less) monitoring well screen intervals. Procedures for use of diffusion bag samplers are provided in ITRC (2004).

#### In Situ Groundwater Sampling

In situ (depth-specific) sampling during drilling of monitoring wells can be performed using a HydroPunch  $^{\text{TM}}$ , SimulProbe, or BAT  $^{\text{TM}}$  sampler in order to assess the vertical extent of 1,2,3-TCP groundwater contamination. However, given the depth to groundwater in the central portion of SGV Area 3 (275 to 300 feet bgs), the cost to use this approach as a screening technique would be prohibitively expensive and time consuming.

#### 4.2 Soil

Soil samples for analysis should be collected in Encore samplers to reduce 1,2,3-TCP losses from volatilization. Direct push samples collected in stainless steel or brass sleeves should be sealed with Teflon tape, foil, and plastic end caps. For samples of loose soil, pack the soil tightly into a 4-ounce glass jar and close the cap tightly. It should be noted that given the moderate volatility of 1,2,3-TCP, surface soil samples are unlikely to contain detectable concentrations of 1,2,3-TCP. Consequently, an alternative approach to characterizing concentrations of 1,2,3-TCP in soil, for example during screening-level investigation of a site, would be to use heated soil head space field analyses. All samples should be placed on ice immediately and maintained at 4°C prior to analysis.

The selection of subsurface samples for submittal to a laboratory for 1,2,3-TCP analysis can be targeted based on headspace concentrations, visible staining, or odor. Concentrations of 1,2,3-TCP are expected to be higher in fine-grained materials (e.g., silt), than coarse-grained materials (e.g., gravel), where it would be more easily volatilized in the vadose zone or be more rapidly flushed away by groundwater flow in the saturated zone (i.e., below the groundwater table).

#### 4.3 Soil Gas

Little information is available on the effectiveness of soil gas surveys in assessing sources and releases of 1,2,3-TCP and the extent of 1,2,3-TCP soil contamination. A soil gas survey was completed during 2003 at the Aeroquip Corporation in the San Fernando Valley Superfund Site (Area 1 - North Hollywood and Burbank-OU), California (Tetra Tech, 2003), however). However, 1,2,3-TCP was essentially not detected in any soil gas samples above the detection limit of 1 µg/L (Appendix D). For this reason, until additional sampling results are produced, soil gas surveys are not expected to be particularly effective for identifying 1,2,3-TCP sources. A combination of subsurface soil samples, groundwater sampling, and potentially soil gas sampling near suspected releases is expected to be the most effective approach to identify 1,2,3-TCP sources.

LARWQCB-lead investigations at facilities in the SGV where suspected releases of VOCs (e.g., TCE or PCE) have occurred typically begin with a soil gas survey. Because 1,2,3-TCP is less volatile than PCE or TCE (see Appendix A), collecting soil gas samples on a sampling grid for screening of a facility as a potential source is not a suitable way to investigate a facility where 1,2,3-TCP may have been used or released into the subsurface. Instead, evaluation of operations at the facility or business should be known, so that collection of soil gas samples can be focused on those areas where elevated subsurface concentrations associated with a release are likely to occur.

## 5. Analytical Methods

A summary of recommended analytical methods for the analysis of 1,2,3-TCP in soil, soil gas, and groundwater, is provided in this section.

#### 5.1 Groundwater

Because accepted collection methods (see Section 4) generally result in samples from monitoring or production wells with low levels of turbidity (e.g., less than 5 nephelometric turbidity units [NTUs]), most groundwater samples can be analyzed using methods developed for (unfiltered) drinking water. To allow laboratories to meet the DHS detection limit for reporting purposes (DLR) of 0.005  $\mu$ g/L for 1,2,3-TCP (consistent with the NL of 0.005  $\mu$ g/L), DHS developed two analytical methods which are DHS-approved for analysis of water (including groundwater) samples for public (drinking) water systems (see below). In total, DHS has approved the use of four analytical methods for the analysis of 1,2,3-TCP in water: DHS PT-GC/MS, DHS LLE-GC/MS, EPA 504.1, and EPA 551.1. These four methods are summarized in Table 5-1. Based on results in EPA's San Gabriel Basin database, samples from essentially all of the active production wells in SGV Area 3, most of which are used to supply (unfiltered) drinking water, have been analyzed using one of these DHS methods (see Appendix C, UCMR).

TABLE 5-1
DHS-Approved Analytical Methods for 1.2.3-TCP in Water

Method	Detection Limit (μg/L)	Sample Container	Holding Time	Approximate Cost per Sample
DHS PT-GC/MS <sup>a</sup>	0.005	40-mL vial. HCl to pH <2: cooled to 4°C	14 days	\$150

TABLE 5-1
DHS-Approved Analytical Methods for 1,2,3-TCP in Water

Method	Detection Limit (μg/L)	Sample Container	Holding Time	Approximate Cost per Sample
DHS LLE-GC/MS	0.005	1-L amber bottle; cooled to 4°C	<ul><li>14 days before extraction;</li><li>24 hours for extract analysis</li></ul>	\$225
EPA 504.1	0.02	40-mL vial with sodium thiosulfate; cooled to 4°C	<ul><li>14 days before extraction;</li><li>24 hours for extract analysis</li></ul>	\$85
EPA 551.1	0.008	60-mL vial with ammonium chloride; cooled to 4°C	<ul><li>14 days before extraction;</li><li>14 days for extract analysis</li></ul>	NA

<sup>&</sup>lt;sup>a</sup>Used by USEPA Region 9 for groundwater monitoring samples.

#### **DHS Analytical Methods**

Due to the extremely low DHS detection limit for reporting purposes (DLR) required to meet the notification level for 1,2,3-TCP (0.005  $\mu g/L$  or 5 ng/L), EPA methods 502.2, and 524.2 are not applicable for determining this compound in drinking water, even though 1,2,3-TCP is listed as an analyte in the method. Consequently, the DHS Sanitation and Radiation Laboratories (SRL) developed two gas chromatography/mass spectroscopy (GC/MS) methods (Purge and Trap GC/MS and Liquid-Liquid Extraction GC/MS) that are capable of 1,2,3-TCP quantification at the DLR. In February 2002 CA DHS published the two new analytical methods, listed below.

- Determination of 1,2,3-Trichloropropane in Drinking Water by Purge and Trap Gas Chromatography/Mass Spectrometry (DHS PT-GC/MS). <a href="http://dhs.ca.gov/ps/ddwem/chemicals/unregulated/TCPbyPT-GCMS.pdf">http://dhs.ca.gov/ps/ddwem/chemicals/unregulated/TCPbyPT-GCMS.pdf</a>.
- Determination of 1,2,3-Trichloropropane in Drinking Water by Continuous Liquid-Liquid Extraction and Gas Chromatography/Mass Spectrometry (DHS LLE-GC/MS). <a href="http://dhs.ca.gov/ps/ddwem/chemicals/unregulated/TCPbyLLE-GCMS.pdf">http://dhs.ca.gov/ps/ddwem/chemicals/unregulated/TCPbyLLE-GCMS.pdf</a>.

Both methods use GC/MS in the selective ion monitoring (SIM) mode and isotope dilution to meet the low DLR. Quantitation is performed using isotope dilution with TCP-D5. VOCs which co-elute or overlap with TCP or TCP-D5, and which yield the same fragment ions as TCP or TCP-D5, can be a major source of error in both these methods. Due to the extreme sensitivity of these methods, even low abundances of these ions can result in severe interference when the interfering compound is present at sufficiently high concentrations. The following compounds have the potential to interfere: trans-1,4-dichloro-2-butene (m/z 75 ion), isopropylbenzene (m/z 75 ion), o-xylene (m/z 79 ion).

#### EPA Methods 504.1 and 551.1

Laboratories performing analysis of 1,2,3-TCP in groundwater may use one of the DHS GC/MS methods above. Alternatively, EPA methods 504.1 or 551.1 may also be used if the laboratory can demonstrate that the method is capable of achieving the DLR of 0.005  $\mu g/L$  without method modification.

A laboratory using EPA method 504.1 or 551.1 will be required to do the following:

Demonstrate that it can achieve the DLR,

- Demonstrate that the laboratory blank is not contaminated, and
- Confirm a positive detection that is at or above the DLR either by a second column analysis, or by one of the DHS GC/MS methods above. This confirmation will be required only for the initial characterization of a water source. Confirmation will not be required on subsequent analyses of the same water source.

It should be noted that 1,2,3-TCP detection in a sample that has a high total dissolved solids (TDS) or VOC content, or otherwise precludes unambiguous confirmation, should be confirmed with one of the DHS GC/MS methods above.

The list of laboratories that are certified by DHS under the Environmental Laboratory Accreditation Program (ELAP) to perform 1,2,3-TCP analysis in drinking water is available at <a href="http://www.dhs.ca.gov/ps/ls/elap/html/lablist.htm">http://www.dhs.ca.gov/ps/ls/elap/html/lablist.htm</a>.

#### **Older Analytical Methods**

Listed in Table 65-2 are other analytical methods that have been used in the past for the analysis of 1,2,3-TCP in water or are currently in use for which 1,2,3-TCP is not the primary target analyte. The detection limits of these methods are considerably higher than the DHS DLR of 0.005  $\mu$ g/L.

TABLE 65-2
Other Analytical Methods for 1,2,3-TCP in Water

Method	Detection Limit	Sample Container	Holding Time	Approximate Cost per Sample
EPA 524.2	0.03 μg/L	40-mL vial with ascorbic acid <sup>a</sup> ; HCl to pH <2; cooled to 4°C	14 days	\$225 to \$275
502.2	0.4 μg/L	40-mL vial with ascorbic acida; HCl to pH <2; cooled to 4°C	14 days	\$110 to \$275

<sup>&</sup>lt;sup>a</sup>Use of ascorbic acid is recommended in samples collected from some public drinking water systems to remove any chlorine that may be in the water. Ascorbic acid is a very weak acid that is not be suitable for lowering the pH of the sample (HCl is instead used for that purpose).

#### 5.2 Soil

Recommended analytical methods for the analysis of 1,2,3-TCP in soil samples are provided in Table  $\frac{75-3}{2}$ .

TABLE 75-3 Analytical Methods for 1,2,3-TCP in Soil

Method	Detection Limit (μg/kg)	Sample Container	Holding Time	Approximate Cost per Sample
EPA 8021B	1	Brass or SS sleeve <sup>a</sup> , cooled to 4°C	14 days; otherwise analysis must be completed within 48 hours if samples are not frozen prior to the expiration of the 48-hour period. Sample should not be	\$150

TABLE 75-3
Analytical Methods for 1,2,3-TCP in Soil

Method	Detection Limit (μg/kg)	Sample Container	Holding Time	Approximate Cost per Sample
	(1-0-0)		frozen below – 20°C due to potential problems with seals and the loss of constituents upon sample thawing.	
EPA 8260B	5	Brass or SS sleeve <sup>a</sup> , cooled to 4°C	14 days; otherwise analysis must be completed within 48 hours if samples are not frozen prior to the expiration of the 48-hour period. Sample should not be frozen below - 20°C due to potential problems with seals and the loss of constituents upon sample thawing.	\$225 to \$350
EPA 8270C	1	Brass or SS sleeve, cooled to 4°C	14 days; otherwise analysis must be completed within 48 hours if samples are not frozen prior to the expiration of the 48-hour period. Sample should not be frozen below - 20°C due to potential problems with seals and the loss of constituents upon sample thawing.	\$195

 $<sup>^{</sup>a}$ To minimize analyte loss, EPA recommends collecting a soil sample in an Encore sampler, or extruding the sample into an empty sealed vial, cooling to  $4 \pm 2^{\circ}$ C for no more than 48 hours, then freezing to -7°C upon laboratory receipt.

#### 5.3 Soil Gas

Soil gas surveys have been used to investigate suspected 1,2,3-TCP sources in groundwater basins like the SGV to a very limited extent. A contractor performed a soil gas investigation at an aircraft industry facility in the San Fernando Valley Superfund Site (Area 1 - North Hollywood and Burbank OU in Southern), California. Soil vapor samples were analyzed using an unpublished procedure (Pavlick, 2004). Soil vapor samples were analyzed utilizing a and with a GC with a MS detector (GC/MS) in both "open scan" and SIM modes: (Pavlick, 2004). Soil gas samples were collected as either whole samples in SUMMA canisters or Tedlar bags, or on charcoal/tenax tubes. Soil gas samples were analyzed either directly or using a tenax trap to collect 1,2,3-TCP prior to desorbption into the GC/MS. The sensitivity of this unpublished GC/MS SIM method was approximately 0.1 to 0.2 ppbV.

In this case, collection probes for the soil gas samples were placed at depths 20 to 30 above the groundwater table near a monitoring well in which 1,2,3-TCP had been previously detected of up to  $200 \,\mu g/L$  (Tetra Tech, 2003). Soil gas samples collected from these probes contained either very low, or no detectable, concentrations of 1,2,3-TCP. The contractor performing the analysis noted that the method was reliable, but not robust enough to be used as a stand-alone procedure, because groundwater and soil analytical results did not correlate well to the soil gas analytical results. Ultimately, the contractor concluded that, until further soil gas analysis research was performed, soil gas analysis for 1,2,3-TCP should

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be combined with 1,2,3-TCP analysis of samples of soil and groundwater from the facility, to have sufficient understanding of the presence/absence of 1,2,3-TCP.

Methods for soil gas analysis should be a function of the sampling method chosen (i.e., passive or active) and the intended use of the data collected. Field analysis using portable instrumentation, such as GC and/or MS, may be performed, usually by a mobile laboratory, or samples may be shipped to an off-site laboratory. Off-site laboratory analysis is generally more expensive, but reliable, because more rigorous quality control procedures are in place.

Currently, there are limited information and data regarding the sampling and analysis of 1,2,3-TCP in soil vapor/ambient air. NIOSH method 1003 is currently used for monitoring worker exposure in ambient air. The NIOSH method for off-site laboratory analysis involves extraction of the sample on a solid sorbent with carbon disulfide, and analysis by GC with a flame ionization detector (FID). The method requires the use of a charcoal tube for sample collection and analysis by a GC/FID, with a reporting limit of roughly 1 ppmV. This method lacks the sensitivity and selectivity required for most facility source investigations. Table 85-4 below summarizes the methods that are available for 1,2,3-TCP analysis of soil gas. Method modifications to meet the project- or site-specific detection limits may need to be evaluated and considered.

TABLE 8<u>5-4</u>
Analytical Methods for 1,2,3-TCP in Soil Gas

Method	Detection Limit	Sample Container	Holding Time	Approximate Cost per Sample
EPA 8260B	1 μg/L - vapor	Amber gas-tight glass bulb or SUMMA canister	4 hours for amber gas-tight glass bulb; 72 hours for SUMMA canister <sup>a</sup>	NA
NIOSH 1003	0.01 mg/ sample	Solid sorbent	None published, but analysis should be done as soon as possible to minimize analyte loss	NA
EPA TO-15	0.050 μg/m <sup>3</sup>	SUMMA canister	30 days	\$125

<sup>&</sup>lt;sup>a</sup>LARWQCB requirement.

### 6 Remediation and Treatment

#### 6.1 Remediation

Only limited information is available on remediation of 1,2,3-TCP contamination. Potential remediation approaches are summarized below in Table  $9\underline{6-1}$ .

**TABLE 96-1**Remediation Approaches for 1,2,3-TCP Contamination

Approach	Media	Description
Pump and Treat	Groundwater	Effective for containment or source control. Not expected to be cost effective for source remediation. See Table 406-2 for groundwater treatment approaches.
In Situ Vacuum	Soil, Soil Gas	Full-scale remediation of soils, bedrock, and groundwater is

TABLE 96-1
Remediation Approaches for 1.2.3-TCP Contamination

Remediation Approaches for 1,2,3-TCP Contamination			
Approach	Media	Description	
Extraction and In Situ Oxidation.	(vapor), and Groundwater	underway at the Tyson Superfund Site near Philadelphia, Pennsylvania, using in situ vacuum extraction of silty clay soils, dual extraction of water and vapor from underlying fractured sandstone, and collection and treatment of seep water. Vapor treatment uses activated carbon adsorption (Pezullo et al., 2005). Oxidants have been injected into the subsurface in areas of DNAPL containing 1,2,3-TCP to oxidize contaminants in the subsurface. The more volatile byproducts from the oxidation reactions are captured by the vacuum extraction system that is designed to recover these byproducts. It should be noted that because the Henry's Law constant for 1,2,3-TCP (3 x 10-4) is below the 10-3 threshold commonly used to assess application of soil vapor extraction (SVE) as a stand-alone remedial alternative, vacuum extraction may not be the most effective remedial approach (see Appendix D, MacKenzie Chemical Works site).	
Dechlorination by Hydrogen Releasing Compounds	Groundwater	Use of Hydrogen Release Compound (HRC®) for in situ treatment of 1,2,3-TCP resulted in 99.9% reduction over 1,000 days at confidential site in California (Reilly, 2005). HRC is a product designed for in situ treatment of chlorinated solvents or any anaerobically degradable substance. HRC slowly hydrolyzes releasing lactic acid, which is utilized by microbes to produce hydrogen, thereby inducing reductive dechlorination.	
Permeable Reactive Barrier (PRB)	Groundwater	1,2,3-TCP has been shown to be reduced by zero-valent iron. Therefore, the application of permeable reaction barrier (PRB) technology may be a viable approach to remediation of a shallow 1,2,3-TCP plume (Focht and Gillham, 1995; Vidic and Pohland, 1996). Others have described the feasibility of using a PRB for remediation of 1,2,3-TCP in groundwater (USEPA, 1998).	
		EnviroMetal Technologies, Inc. (ETI) has performed bench column testing to treat 1,2,3-TCP in groundwater. Treatability testing involved water from a site in California and use of a 100 percent commercially available granular iron supply. The influent concentration of 437 μg/L 1,2,3-TCP declined to non-detectable concentrations during a 12-hour residence time at room temperature (ETI, 2005). Based on this testing, ETI is recommending the application of a granular iron PRB to treat 1,2,3-TCP groundwater contamination.	
		Given the depth to groundwater in SGV Area 3 (275 to 300 feet bgs), a PRB could not be installed via a trench, but would likely need to be installed by injecting the materials into the subsurface via closely spaced wells.	
In Situ Biodegradation	Groundwater	1,2,3-TCP was not readily biodegradable in aerobic biodegradation tests and is only slowly transformed by bacteria under aerobic and anaerobic conditions (WHO, 2003). Bosma (2002) has genetically engineered a strain of bacteria that can utilize 1,2,3-TCP as a food source. However, the microbial activity is insufficient to sustain bacterial growth. Peijnenburg, et al (1998) observed the reductive dehalogenation of 1,2,3-TCP in anaerobic sediments. See Appendix A for additional discussion of 1,2,3-TCP biodegradation.	

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TABLE 96-1
Remediation Approaches for 1,2,3-TCP Contamination

Approach	Media	Description
SERDP Initiatives	Groundwater	The U.S. Department of Defense's Strategic Environmental Response and Development Program (SERDP) sponsors initiatives for innovative remediation approaches. The SERDP currently (April 2005) has a project (CU-1457) listed on their website (http://www.serdp.org/research/Cleanup.html) which involves investigating prospects for remediation of 1,2,3-TCP by natural and engineered abiotic degradation reactions.

#### 6.2 Treatment

Although treatment of 1,2,3-TCP in groundwater is underway at some contaminated sites in the U.S., only limited information regarding the technologies is available at this time. The initial screening of groundwater treatment technologies presented below was prepared based on experience at the <a href="San Fernando Valley Superfund Site">San Fernando Valley Superfund Site</a> (Area 1 - North Hollywood and Burbank OU site in Los Angeles County), California.

TABLE 406-2
Ex-Situ Groundwater Treatment Technology Screening for Removal of 1,2,3-TCP

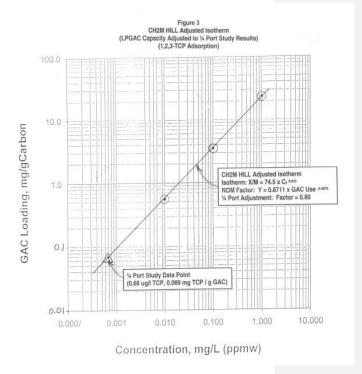
Treatment Technology	Application Performance Opinion	
Air Stripping	Poor	
Liquid-Phase Granular Activated Carbon Adsorption	Very Good	
Advanced Oxidation	Poor	
Biological Reduction	Poor	
Ion Exchange	NA	
Reverse Osmosis	Fair	
Zero Valent Iron Dechlorination	Fair	
NA – Not applicable		

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#### **Key Treatment Technology Discussion:**

Ex-situ treatment using liquid-phase granular carbon adsorption (LGAC) is the technology that is in use for treatment of 1,2,3-TCP in groundwater at the San Fernando Valley Superfund Site (Area 1 - North Hollywood and Burbank-OU.), California.. The isotherm figure to the right presents an isotherm developed for 1,2,3-TCP using site-specific rapid small scale column test data provided by Calgon Corporation and full-scale site data from the San Fernando Valley Superfund Site (Area 1 - North Hollywood and Burbank-OU site), California.

Typical LGAC vessel design flux (5 to 8 gallons per minute (gpm)/square foot) and empty bed contact time (10 minutes) assumptions are used. Treatment of 1,2,3-TCP using LGAC appears to have an unusually long mass transfer zone, which results in earlier breakthrough than most common VOCs (e.g., TCE and PCE).



#### **Advanced Oxidation**

The HiperOxidation<sup>TM</sup> (HiPOx<sup>TM</sup>) process has been in use for treatment of primarily Methyl Tert-Butyl Ether (MTBE), with minor concentrations of 1,2,3-TCP, at the former Marine Corps Air Station (MCAS) Tustin underground storage tank (UST) Site 222 (NAVFAC, 2003). As of 2003, nearly 2,910 pounds of MTBE and 1 pound of 1,2,3-TCP had been removed from groundwater at the former MCAS Tustin. Based on experience at the former MCAS Tustin, the cost of operating the HiPOx<sup>TM</sup> treatment system is nearly 3 times the cost of operating a LGAC system for treatment of the 1,2,3-TCP groundwater contamination. Addition detail on the operation of the HiPOx system 1,2,3-TCP and other chlorinated solvents in groundwater is provided by Dombeck (2005).

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TRICHLOROPROPANE&edf\_substance\_id=96-18-

4&how\_many=100&drop\_down\_name=Total+environmental+releases&fips\_state\_code=Entire+United+States&sic\_2=All+reporting+sectors.

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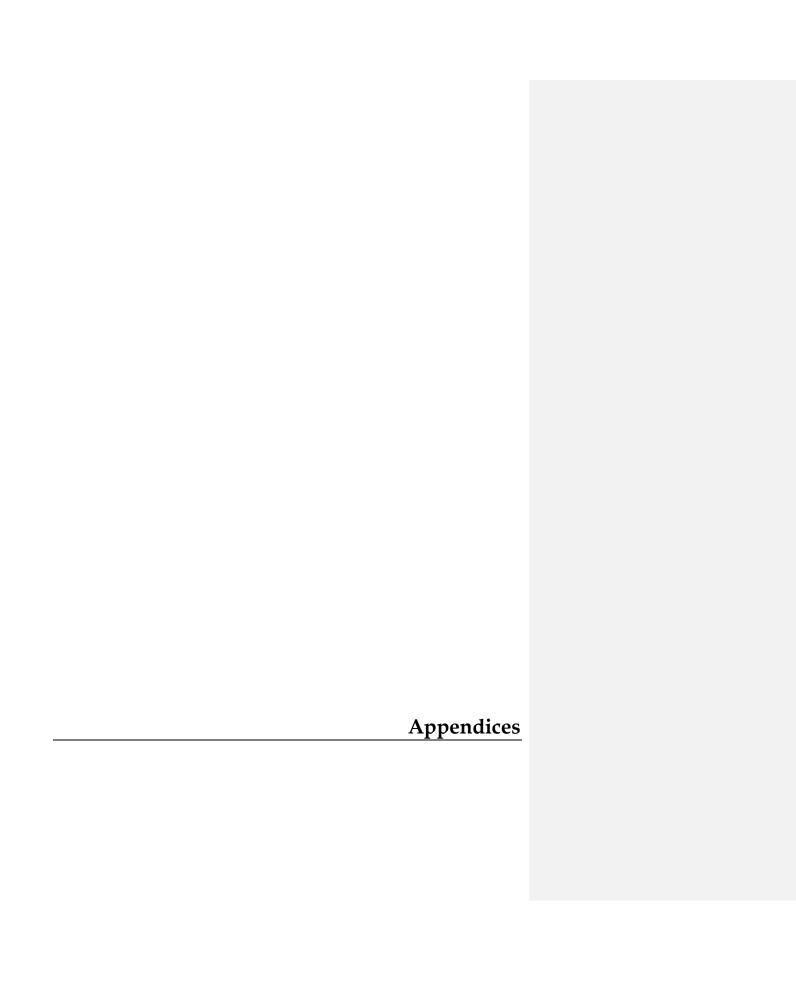
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#### APPENDIX A

# **Chemical Properties/Environmental Fate and Transport**

## **Chemical Properties**

1,2,3-Trichloropropane (1,2,3-TCP), which can be referred to using a variety of chemical names and identifiers (Table A-1), is a non-polar chlorinated alkane that is soluble in alcohol, ether, and chloroform and is slightly soluble in water. It dissolves oils, waxes, fats, chlorinated rubber and numerous resins. It is sensitive to prolonged exposure to light and heat. It is reactive with chemically active metals, strong caustics, and oxidizers. When heated to decomposition, it yields highly toxic fumes of carbon monoxide, carbon dioxide, hydrogen chloride, phosgene, and other chlorinated compounds. Table A-2 lists chemical properties of 1,2,3-TCP and how these properties relate to the behavior of 1,2,3-TCP in the environment.

Formula: C<sub>3</sub>H<sub>5</sub>Cl<sub>3</sub>

#### **Chemical Structure:**

TABLE A-1 Chemical Names and Identifiers

Item	Description	Comments
Synonyms	allyl trichloride	These may turn up during investigation into
	glycerin trichlorohydrin	potential 1,2,3-TCP uses at Area 3 facilities/businesses
	glycerol trichlorohydrin	
	glyceryl trichlorohydrin	
	trichlorohydrin	
	trichloropropane	
	1,2,3-TCP	
	TCP	
Identifiers	United Nations No.: 2810	These may turn up during investigation into
	Chemical Abstract System (CAS) Registry No.: 96-18-4	potential 1,2,3-TCP uses at Area 3 facilities/businesses
	Chemical Hazard Response Information System (CHRIS): TCN	
	Storet No.: 7743	

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TABLE A-2 Chemical Properties of 1,2,3-TCP

Property	Value	Reference	Environmental Efficacy	
Molecular Weight	147.44 g	Verschueren, 1996		
Density at 20°C (Water = 1)	1.42 g/cm <sup>3</sup>	Verschueren, 1996	More dense than groundwater, can act as DNAPL.	
Boiling Point	156 °C	WHO, 2003	Liquid at room temperature	
Melting Point	-14.7 °C	WHO, 2003		
Vapor Pressure at 25°C	3.1 mm Hg	ATSDR, 1992	Evaporates quickly at ambient temperatures; can be removed from surface water by evaporation.	
Air Saturation at 20°C	16 g/m <sup>3</sup>	Verschueren, 1996		
Relative Vapor Density (Air=1)	5.1	WHO, 2003	Vapor is more dense than air, can accumulate above the water table.	
Henry's Law Constant at 25°C	2.8 to 4.4 mol/kg*bar	NIST database	Volatile, but does not volatilize as readily as PCE, TCE; moderate volatilization from either dry or moist soil to the atmosphere.	
	22.83 Pa-m³/mol	WHO, 2003		
	3.17 x 10 <sup>-4</sup> atm-m <sup>3</sup> /mol	ATSDR, 1992		
Solubility at 25°C	1.75 g/L	WHO, 2003	Relatively insoluble, but up to 1,750 mg/L (1,750,000 µg/L) may be present in water.	
Octanol/Water Partition	2.54 (calculated)	WHO, 2003	The low Kow value indicates	
Coefficient (log K <sub>ow</sub> )	2.27 (measured)	WHO, 2003	that 1,2,3-TCP is mobile in the environment.	
	1.98	ATSDR, 1992		
Organic Carbon Partition	68	NYSDEC (2005)	Is expected to display high mobility in soil, and therefore has the potential to leach into groundwater primarily as 1,2,3-TCP.	
Coefficient (log K <sub>oc</sub> )	98 (calc. from solubility)	Lyman, et al. (1982)		

Table A-3 identifies the physical properties of 1,2,3-TCP relative to the physical properties of PCE, TCE, and 1,4-dioxane. Based on the organic carbon partition coefficients shown in Table A-3, 1,2,3-TCP is more mobile in groundwater than PCE and TCE. Vapor pressure and Henry's Law Constant values further indicate that 1,2,3-TCP is more difficult to detect in soil gas than PCE and TCE. If present in vadose zone soil, 1,2,3-TCP will preferentially reside in pore moisture. Once in the environment, 1,2,3-TCP is likely to be as resistant to aerobic degradation as PCE and/or TCE.

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#### **Environmental Fate and Transport**

#### **Abiotic Transformations**

A calculated half life of 27.2 to 30.5 days for 1,2,3-TCP in the atmosphere has been reported. Therefore, 1,2,3-TCP released in the atmosphere might undergo very slow degradation in the presence of a sufficient concentration of photochemically-produced hydroxyl radicals. Hydrolysis of 1,2,3-TCP in air appears to be of minor importance, with calculated half lives of 44 and 74 years (WHO, 2003).

#### **Biotransformation and Degradation**

In aerobic biodegradation tests,1,2,3-TCP was not readily biodegradable. In a preliminary study, the co-oxidative transformation of 1,2,3-TCP by the ammonia oxidizing bacterium Nitrosomonas europaea was shown (Vanelli et al., 1990). More recent studies employing the methanotroph Methylosinus trichosporium demonstrated that 1,2,3-TCP is cometabolized to a range of different chemicals, such as chlorinated propanols (Bosma and Janssen, 1998). However, attempts to isolate cultures to utilize 1,2,3-TCP as a sole source of carbon and energy have failed (WHO, 2003). Peijnenburg et al (1998) observed the reductive transformation of 1,2,3-TCP in anaerobic sediments, and determined that reductive dehalogenation was the sole reaction taking place. Anderson et al. (1991) reported a lack of biodegradation of 1,2,3-TCP in clay loam.

For soil fumigants containing 1,3-dichloropropene and chloropropanes, biodegradation appears to be much more significant for 1,3-dichloropropene than either 1,2-dichloropropane or 1,2,3-TCP. 1,3-Dichloropropene in the vapor-phase, will react with air, as well as volatilize, biodegrade, and hydrolyze in soils and surface waters. Once 1,2-dichloropropane and 1,2,3-TCP have entered the groundwater, further breakdown products are unlikely to be generated, because both compounds are resistant to hydrolysis and biodegradation.

1,2,3-TCP is not readily biodegraded and is only slowly transformed by bacteria under aerobic and anaerobic conditions. And, 1,2,3-TCP has not been shown to bioaccumulate.

# **Uses and Manufacturers**

### Uses

1,2,3-TCP has been used as a solvent for hydrophobic compounds and resins, as a paint and varnish remover, and a degreasing agent up to approximately the 1950's and perhaps the 1960's. Another documented use of 1,2,3-TCP was as a "branching agent" in polysulfide polymers, which were used as sealants for aircraft fuel tanks and as a binder for rocket fuel (Kirk Othmer Encyclopedia of Chemical Technology, 2004). 1,2,3-TCP has also been used in a mixture with 1,3-dichloropropene and 1,2-dichloropropane as soil fumigants to control nematodes affecting agriculture. 1,2,3-TCP is currently used primarily as a chemical intermediate in the production of polysulfone liquid polymers and dichloropropene, synthesis of hexafluoropropylene, and as a cross-linking agent in the synthesis of polysulfides. It is also produced in significant quantities as a by-product of the production of other chlorinated compounds, including epichlorohydrin.

#### Solvent

1,2,3-TCP had been used in the past primarily as a solvent for paint and varnish removal, as a cleaning and degreasing agent, and as a cleaning and maintenance solvent. No current information is available to indicate that it continues to be used for these purposes (National Toxicity Program, 2005).

#### **Soil Fumigants**

Pre-1980's, agricultural use of chloropropane-containing soil fumigants for use as pesticides and nematicides was prevalent in the U.S. Some soil fumigants, which contained a mixture of primarily 1,3-dichloropropene and 1,2-dichloropropane, and in which 1,2,3-TCP was a minor component (e.g., trade name of D-D), were marketed for the cultivation of a variety of crops including: citrus fruits, pineapple, soy beans, cotton, tomatoes, and potatoes. D-D is no longer available in the U.S., and has been replaced with Telone II, which reportedly contains as much as 99 percent 1,3-dichloropropane and up to 0.17 percent by weight of 1,2,3-TCP (Zebarth, et al. 1998). Before 1978, approximately 55 million pounds/year of 1,3-dichloropropene were produced annually in the U.S., and approximately 20 million pounds/year of 1,2-dichloropropene and 1,2,3-TCP were produced as by-products in the production of 1,3-dichloropropene. Over two million pounds of pesticides containing 1,3-dichloropropene were used in California alone in 1978.

#### Aircraft Fuel Tank Sealers

Another documented use of 1,2,3-TCP was as a "branching" or curing agent in polysulfide polymers (Kirk Othmer Chemical Encyclopedia, 2001). Polysulfide polymers were used as the "standard sealant for virtually all aircraft fuel tanks and bodies" and "one of the first large-scale applications of the liquid polysulfides was as a binder for rocket fuel." Kirk Othmer's (2001) tables list properties of a number of Morton Thiokol LP series of polysulfide

polymer-based sealers, with concentrations of the branching agent (1,2,3-TCP) ranging from 0.5 to 2.0 percent. Liquid polysulfide polymers are used mainly as sealants, including for double paned windows, boat hulls and decks, printing rolls, integral aircraft fuel tanks, and aircraft bodies.

#### **Chemical Intermediates**

By the early 1980's, approximately 95% of chloropropanes were being used as chemical intermediates. Chemical intermediates are industrial chemicals that are used as the starting point to produce other chemicals. 1,2,3-TCP is currently used as an intermediate in the production of polysulfone liquid polymers, the synthesis of hexafluoropropylene, and as a cross-linking agent in the synthesis of polysulfides.

Polysulfone liquid polymers are used in the following industries: aerospace, automotive, consumer goods, electrical and electronic, health care, and in industrial equipment, such as compressor and pump valve components. Hexafluoropropylene is a fluorointermediate that is a key building block required to produce Teflon fluoropolymers and has applications in the agrochemical, electronics, dyes/pigments, pharmaceutical, and specialty polymer markets. Polysulfides are used as catalyst sulfidation agents and in the formulation of lubricant additives for extreme pressure functionality.

#### **Manufacturers**

1,2,3-TCP is manufactured as a stand-alone product in the U.S. It is also produced in significant quantities as an unwanted byproduct of the production of other chlorinated compounds such as epichlorohydrin, and is used internally by manufacturers as an intermediate in the production of other chemicals such as polysulfone and epoxy resins (see Table B-1 below).

TABLE B-1
1.2.3-TCP Manufacturing Information

Item	Description	Comments
Current U.S. Manufacturers	Dow Chemical Company, Freeport, Texas Shell Chemical Company, Deer Park, Texas	Primary source of 1,2,3-TCP in the U.S. and potential supplier for facilities or businesses in Area 3
Bulk Uses/Origins	External sale  Unwanted byproduct of the production of other chlorinated compounds, including dichloropropene, propylene chlorohydrin, dichlorohydrin, glycerol, and especially epichlorohydrin  Chemical intermediate	The majority (>80%) of the 1,2,3-TCP produced in the U.S. is a byproduct of epichlorohydrin production and is incinerated onsite (WHO, 2003). There are 20 to 30 epichlorohydrin facilities in North America, Europe, and Asia.
Production	U.S. annual production of 1,2,3-TCP in 2000 estimated to be 9,000 to 14,000 tons 50,000 tons of 1,2,3-TCP is produced globally as a byproduct of other chlorinated compounds (WHO, 2003)	

**TABLE B-1** 1,2,3-TCP Manufacturing Information

Item	Description	Comments
Current U.S. Manufacturers	Dow Chemical Company, Freeport, Texas Shell Chemical Company, Deer Park, Texas	Primary source of 1,2,3-TCP in the U.S. and potential supplier for facilities or businesses in Area 3
Bulk Uses/Origins	External sale  Unwanted byproduct of the production of other chlorinated compounds, including dichloropropene, propylene chlorohydrin, dichlorohydrin, glycerol, and especially epichlorohydrin  Chemical intermediate	The majority (>80%) of the 1,2,3-TCP produced in the U.S. is a byproduct of epichlorohydrin production and is incinerated onsite (WHO, 2003). There are 20 to 30 epichlorohydrin facilities in North America, Europe, and Asia.
History	Production of chloropropanes (e.g., 1,2,3-TCP, 1,2-dichloropropane, etc.) for external sale starting to be curtailed by the early 1980's  Chloropropanes were no longer sold for consumer use (as solvents) and, production of 1,2-dichloropropane (and 1,2,3-TCP) for agricultural use by DOW Chemical Co. was discontinued by 1983.	

#### APPENDIX C

# **Regulatory Levels**

A summary of regulatory levels for 1,2,3-TCP is provided below, followed by more detailed text descriptions.

## **California Notification Level**

In May 1999, the California Department of Health Services (DHS) Division of Drinking Water and Office of Health Hazard Assessment announced an action level (now referred to a notification level [NL]) of 0.005  $\mu g/L$  for 1,2,3-TCP<sub>7</sub>. The NL is based on the categorization of 1,2,3-TCP as a probable human carcinogen, on the discovery of 1,2,3-TCP in groundwater at the San Fernando Valley Superfund Site (Area 1 - North Hollywood and Burbank OU in Los Angeles County), California, and over a concern that the chemical might find its way into public drinking water supplies.

#### **UCMR Monitoring**

In 2001, to obtain information about the presence of 1,2,3-TCP in drinking water sources, DHS adopted a regulation that included 1,2,3-TCP as an unregulated contaminant for which monitoring is required (UCMR). For this monitoring, DHS developed protocols for analytical methods for 1,2,3-TCP at levels comparable to the NL of 0.005  $\mu$ g/L. Monitoring under the UCMR regulation was to have been completed by the end of 2003.

The adoption of these regulations occurred before the availability of a method capable of achieving 1,2,3-TCP's detection limit reporting (DLR) of 0.005  $\mu g/L$ . Some utilities proceeded with monitoring, using laboratory analyses with higher DLRs. Unfortunately, findings of non-detect (ND) with a DLR higher than 0.005  $\mu g/L$  do not provide DHS with adequate information needed for possible standard setting. DHS' Sanitation and Radiation Laboratory developed an adequate analytical method and some commercial laboratories are able to achieve the 0.005- $\mu g/L$  DLR with either EPA method 504.1 or 551.1. Therefore, any utility with 1,2,3-TCP findings of ND with reporting levels of 0.010  $\mu g/L$  or higher should perform follow-up sampling of representative sources for analysis using a method with a 0.005- $\mu g/L$  DLR.

#### Notification of Exceedence of NL

A new law, effective January 1, 2005, requires that public water systems notify local governing bodies (i.e., city councils and county boards of supervisors) when NLs or MCLs for contaminants in drinking water supplies are exceeded. Even if notification occurred prior to that date under previous and different requirements, water systems should familiarize themselves with the new requirements for information to be provided in such a notice and determine whether a new notice should be provided to the governing bodies.

# **EPA Region 9 PRGs**

EPA Region 9 publishes Preliminary Remediation Goals (PRGs) for guidance in performing site remediation, feasibility studies, and risk assessments. PRGs for 1,2,3-TCP are provided with cancer and non-cancer assumptions in Table C-1 (EPA Region 9, October 2004).

#### APPENDIX D

# Documented Occurrences of 1,2,3-TCP Environmental Contamination in the U.S.

1,2,3-TCP may have been released to the environment as a result of its manufacture, formulation, and use as a solvent and extractive agent, paint and varnish remover, cleaning and degreasing agent, cleaning and maintenance agent, and chemical intermediate. Releases may occur as a result of disposal of products that contain the chemical or through agricultural land use applications of certain soil fumigants that are known to contain 1,2-dichloropropane and 1,2,3-TCP. In these instances, the fumigant was injected into the root zone, after which the soil was compacted to enhance retention of the vapor. Releases may have also occurred through the disposal of 1,2,3-TCP-containing sewage sludge from municipal sewage treatment plants.

1,2,3-TCP groundwater contamination has been detected at sites where the manufacture or use of 1,2,3-TCP containing chemicals occurred and at locations that used 1,2-dichloropropane as a soil fumigant (in which 1,2,3-TCP was an impurity). Information on the occurrence of 1,2,3-TCP at these sites may be of use in identifying and investigating potential sources in SGV Area 3 and is presented below.

## **Application of Soil Fumigants**

Contamination of groundwater by 1,2,3-TCP as a result of soil fumigants has been observed in California, Hawaii, and British Columbia.

#### Central Valley, California

1,2,3-TCP groundwater contamination associated with the use of 1,2-dichloropropane as a soil fumigant was observed in the Central Valley of California (City of Shafter, 2000). In 1999, 1,2,3-TCP was detected in five of six active water supply wells at concentrations ranging from 0.02 to 0.11  $\mu g/L$  (Howe, 1999). 1,2,3-TCP was found in groundwater from all wells where 1,2-dichloropropane was detected. Although 1,3-dichloropropene had been applied heavily (thousands of pounds per section), little to none showed up in groundwater from the Merced and Visalia DHS Districts. This was postulated to be due to fact that 1,3-dichloropropene, an unsaturated alkane, would be more easily biodegraded than 1,2-dichloropropane and 1,2,3-TCP, both of which are saturated hydrocarbons. In summary the presence of 1,2,3-TCP was positively correlated with 1,2-dichloropropane, but not with 1,3-dichloropropene.

The California Department of Pesticide Regulation advised that 1,2,2-TCP should also be analyzed where 1,2-dichloropropane and 1,2,3-TCP were detected in groundwater, as it is a byproduct of the manufacture of 1,3-dichloropropene.

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## **Occurrence at Industrial Sites**

#### San Gabriel Valley Superfund Sites, California

Specific sources of 1,2,3-TCP contamination in groundwater in the SGV have not been identified. However, based on results in EPA's San Gabriel Basin database, 1,2,3-TCP concentrations in groundwater at the Wynn Oil facility in the Baldwin Park OU have been as high as 46,000 ng/L and 1,2,3-TCP has been detected in groundwater downgradient of the Wynn Oil facility at 10,000 ng/L (beneath the Aerojet Electrosystems facility). 1,2,3-TCP was also detected in groundwater at the Spectrol Electronics facility in the Puente Valley OU at a concentration of 54,000 ng/L. Because groundwater samples at these facilities were analyzed before mid-1995, confirmation sampling using more recent analytical methods (see Section 5) may be warranted. 1,2,3-TCP has also been detected in groundwater downgradient of the TRW Benchmark facility in the Puente Valley OU at up to 44 ng/L (in October 2003).

#### **Burbank Operable Unit Superfund Site, California**

The use of 1,2,3-TCP for aircraft fuel tank sealers is suspected to be one of the sources of 1,2,3-TCP groundwater contamination in the Burbank OU at the San Fernando Valley Superfund Site in Los Angeles County (Area 1 - North Hollywood and Burbank), California. 1,2,3-TCP was detected in groundwater from 9 of the 39 monitoring wells in the Burbank OU, with concentrations ranging from 0.19  $\mu g/L$  to 170  $\mu g/L$  (Tetra Tech, 2003). The highest concentrations of 1,2,3-TCP occurred in samples collected from near the groundwater table. An area of 1,2,3-TCP groundwater contamination exceeding 0.1  $\mu g/L$ , appearing to originate near the Burbank-Glendale-Pasadena Airport and extends approximately 5,000 downgradient, was generally defined. Lockheed Martin Corporation maintained operations numerous locations adjacent to the airport and had at least two tanks (3,000 and 12,000 gallons) containing aircraft fuel tank sealant at a facility (Plant B-5) south of the airport. At Lockheed Martin's B-6 plant, east of the airport, a small portion of the subsurface soil samples were analyzed for 1,2,3-TCP, and only one sample contained detectable 1,2,3-TCP (1,500  $\mu g/kg$  at a depth of 50 feet bgs). The sample was collected close to a building previously used for testing of aircraft fuel system components at the B-6 plant.

Tetra Tech (2003) identified the Crane Company – Hydro-Aire Division, where aviation, aeronautical, and missile control systems were manufactured, as another potential source of 1,2,3-TCP in groundwater, presumably on the basis of 200 ug/L of 1,2,3-TCP being measured in a monitoring well at the facility. A soil gas survey was completed during 2003 at the Aeroquip Corporation facility, where assembly and distribution of industrial hoses occurred, in the Burbank OU (Tetra Tech, 2003). Groundwater from the Crane Company – Hydro-Aire Division monitoring well downgradient of this facility contained 200 µg/L 1,2,3-TCP, so the Aeroquip Corporation facility was thought to be a potential source of 1,2,3-TCP observed in groundwater. Fifty-four soil gas samples were analyzed for 1,2,3-TCP, however 1,2,3-TCP was essentially not detected in any soil gas samples above the detection limit of 1 µg/L. A trace concentration close to the method detection limit of 0.2 µg/L was observed in only one sample (Pavlick, 2004). Both the Crane Company – Hydro-Aire Division and Aeroquip Corporation facilities are located downgradient of Lockheed Martin's B-6 plant.

#### MacKenzie Chemical Works, New York

At the former MacKenzie Chemical Works Site in Central Islip, Suffolk County, New York, concentrations of 1,2,3-TCP up to 3,900 μg/L in lagoon water and up to 8,900 μg/L in offsite groundwater (600 feet downgradient) were observed, along with lower concentrations of TCE, PCE, and benzene, toluene, ethylbenzene, and xylene (BTEX) compounds (ATSDR, 2004). MacKenzie used the property from 1948 to 1987 for the manufacture of various chemical products, including fuel additives and metal acetylacetonates. MacKenzie stored 1,2,3-TCP in three 10,000-gallon tanks on the property. Other historical waste sources include aboveground storage tanks, leaking drums, waste lagoons, cesspools, and storm water drywells. The lagoons, cesspools, and drywells were sampled and found to contain contaminants attributable to facility operations, including 1,2,3-TCP at concentrations up to 20,400 μg/kg. Soil vapor concentrations of 1,2,3-TCP up to 60-2,200 μg/m³ were detected onsite. EPA's selected a remedy for the site called for thermally-enhanced in situ soil vapor extraction (SVE) for soils contaminated with VOCs, limited excavation and offsite disposal for soils contaminated with semi-volatile organic compounds, demolition of a former laboratory building, and treatment of the groundwater using in situ air sparging with ozone injection.

#### Marine Corps Air Station (MCAS) Tustin, California

This former Marine Corps Air Station (MCAS) in Orange County, California was closed under Base Realignment and Closure (BRAC) and remaining contamination is being remediated prior to base reuse. The proposed plan for OU-1A (the area of TCE and 1,2,3-TCP groundwater contamination at the former MCAS Tustin) describes hydraulic containment with soil hot spot removal as the final remedy. The Department of the Navy is currently treating MTBE, the primary contaminant in groundwater, and 1,2,3-TCP, using in situ chemical oxidation. Pumped groundwater is being treated using the HiPOx treatment system. Both MTBE and 1,2,3-TCP are destroyed using ozone and hydrogen peroxide to create highly reactive hydroxyl radicals, which oxidize organic chemicals (See Section 6 for a discussion of the ongoing remediation). 1,2,3-TCP groundwater contamination at the former MCAS Tustin is associated with a former vehicle maintenance building, and degreasing or cleaning solvents used there may have contained 1,2,3-TCP.

#### Tyson's Dump, Pennsylvania

The Tyson's Dump site, located in Montgomery County, Pennsylvania, is a four-acre abandoned sandstone quarry that was used to dispose of septic and chemical waste from 1962 to 1970. Waste disposal occurred in a series of unlined lagoons. In the 1970s, sludges and liquid wastes, primarily chlorinated and other organic solvents, were dumped into the lagoons (USEPA, May 2004).

Full-scale remediation of soils, bedrock, and groundwater is underway at the Tyson's Dump site. The cleanup involves in situ vacuum extraction in the silty clay soils of the former lagoons and surrounding area, which contains upwards of 250,000 mg/kg total VOCs and semivolatiles. The major contaminants of concern are 1,2,3-TCP, toluene, xylenes and dichlorobenzene, although there are also approximately 20 other compounds identified (See Section 6 for a discussion of the ongoing remediation).

#### Ciba-Geigy Superfund Site, New Jersey

Historic operations at the Ciba-Geigy Superfund Site in Toms River, New Jersey previously included the manufacture of dyes, pigments, resins, and epoxy additives. Sludges and process wastes were stored at a few locations around the former operations, resulting in groundwater contamination by many VOCs, including 1,2,3-TCP. Mean concentrations of the "north plume" at the site were 47 ug/L. The groundwater ROD prescribed a slurry wall, groundwater plume capture wells, a groundwater treatment plant, treated groundwater injection wells, a slurry wall, drum removal, and removal of contaminated soil (USEPA, Sept. 29, 2000). The selected remedial alternative for the source areas at the site is on-site ex-situ bioremediation with off-site treatment/disposal of drummed material (USEPA, June 15, 2000).

The Ciba-Geigy site-specific pilot study performed from October 1999 to April 2000, revealed that ex-situ biological treatment reduced Chemicals of Concern (COCs) concentrations by greater than 90% and reduced the leaching of COCs by more than 99 percent. However, some COCs, such as PCE and 1,2,3 –TCP, did not respond to the aerobic biodegradation process.

## **RCRA Reported Releases**

Known reported releases of 1,2,3-TCP into the environment during 2002 are summarized below (Scorecard website, 2005). Note that the great majority of these releases are to air. The only documented release to water was by Dow Chemical Company (4,225 pounds; not shown in Table D-1).

TABLE D-2
Reported RCRA Releases in the United States During 2002

Rank	Facility	Total Release in 2002 (Pounds)
1.	Deer Park Refining L.P., Deer Park, TX	84,859
2.	Dow Chemical Co., Freeport Facility, FREEPORT, TX	6,520
3.	Resolution Performance Products, Deer Park Plant, Deer Park, TX	5,330
4.	Resolution Performance Products L.L.C., Norco, LA	1,129
5.	Oxy Vinyls L.P. Deer Park, VCM Plant, Deer Park, TX	108
6.	Dow Chemical Co., Louisiana Div., Plaquemine, LA	57

#### APPENDIX E

# **Health Risk Information**

Human exposure to 1,2,3-TCP can occur from inhalation, ingestion of contaminated water, dermal contact with contaminated soil or water, and working in a facility where 1,2,3-TCP is used. 1,2,3-TCP can be measured in blood, urine, and breath. However, it breaks down quickly and leaves the body in breath, urine, and feces.

1,2,3-TCP causes cancer in laboratory animals (US EPA, 1997), which is the basis for the California DHS NL. It is reasonably anticipated to be a human carcinogen (NTP, 2005). In 1999, 1,2,3-TCP was added to the list of chemicals known to the state of California to cause cancer [Title 22, California Code of Regulations, Section 12000].

## **Health Effects**

The main health effect from exposure to 1,2,3-TCP in both animals and people is damage to the respiratory system. Exposure to high levels (100 ppm) of 1,2,3-TCP for a short time can cause central nervous system damage, liver damage and eye, skin and throat irritation. Rats and mice died after breathing air containing 1,2,3-TCP. When swallowed at high levels, rats died from liver and kidney damage. At moderate non-lethal doses, rats had minor liver and kidney damage, blood disorders and stomach irritation. Animals that swallowed low doses for most of their lives developed tumors in several organs. When applied to the skin of rabbits, 1,2,3-TCP caused severe irritation, followed by injury to internal organs.

In the Eighth Report on Carcinogens (1998), 1,2,3-TCP is listed, for the first time, as a substance reasonably anticipated to be a human carcinogen. It is also listed in the Toxic Release Inventory (TRI) as an Occupational Health and Safety Administration (OSHA) carcinogen. However, the Department of Health and Human Services, USEPA, and the International Agency for Research on Cancer have not classified 1,2,3-TCP for carcinogenicity.